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Research Article

Effects of Acid Characteristics of Nanoporous MCM-48 on the Pyrolysis Product Distribution of Waste Pepper Stem

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Nanoporous catalysts Si-MCM-48 and Al-MCM-48 were applied for the first time to the catalytic pyrolysis of waste pepper stem. Pyrolysis experiments were conducted at 550°C using Py-GC/MS to examine the product distribution rapidly. Phenolics were shown to be the most abundant product species of noncatalytic pyrolysis, whereas aliphatic and aromatic hydrocarbons were produced marginally. On the other hand, much larger quantities of furans and aliphatic and aromatic hydrocarbons were produced from the catalytic pyrolysis over MCM-48, while the production of phenolics was suppressed significantly. Al-MCM-48 showed a much higher catalytic activity than Si-MCM-48, which was attributed to its much higher acidity. The results of this study indicate that valuable chemicals can be produced from waste pepper stem using catalytic pyrolysis over an acidic nanoporous catalyst.

1. Introduction

Bioenergy is one of the cheapest renewable energy sources at the state-of-the-art technology level. A variety of types of bioenergy, for example, biodiesel and bioethanol, are widely developed and used over the world accounting for about 15% of the current global energy use, while other renewable energy sources, such as solar energy, cannot compete with conventional fossil energy sources without considerable government subsidy. This is particularly true in South Korea. According to the plan of Korean government for the energy supply in 2030, bioenergy accounts for 30% of total renewable energy supply, following waste energy (33.4%) which is also mostly comprised of organic wastes [1]. Therefore, the effective recycling of waste biomass has a crucial implication in South Korea in terms of both renewable energy supply and waste reduction.

Another important advantage of using waste biomass as a bioenergy source is that it does not cause typical problems raised by energy crops: destruction of forest and reduction of food production [2]. Therefore, a significant attention has been paid to the development of technologies for effective use of organic wastes in energy production [3–5].

Red pepper is widely cultivated over Jeonnam Province of South Korea. The total production of red pepper in South Korea was approximately 1.2 million tons in 2009. Most waste pepper stems are burned or abandoned because it is difficult to compost them or use them as forage.

The thermochemical process in which biomass is heated under an oxygen-free condition to convert biomass to solid, liquid and gaseous fuels is called pyrolysis [6]. Among different pyrolysis techniques, fast pyrolysis refers to the pyrolysis process where residence time in reactor is very short and the temperature rising rate is high. Fast pyrolysis is known to be effective in maximizing the yield of the liquid-phase pyrolysis product, called biooil [7].

Recently we reported the results of a noncatalytic pyrolysis experiment of waste red pepper stem [8]. The most abundant species in biooil obtained from the pyrolysis of waste pepper stem was phenolics, indicating that it might be possible to produce significant amount of aromatics (aromatic hydrocarbons) if catalytic reforming of the biooil

is conducted over adequate catalysts [4, 9]. This study was motivated by the necessity of evaluation of the potential of pepper stem for the production of valuable chemicals such as aromatics by means of catalytic pyrolysis.

Al-MCM-48 is a nanoporous catalyst which is known to be effective in converting large-molecular-mass organic materials to biooil due to its large pore size [10]. In particular, it is known to have high selectivity toward aromatics production [11]. In this study, the catalytic pyrolysis of waste pepper stem over Al-MCM-48 was carried out for the first time. Si-MCM-48 was also used to investigate the effect of the acidity of the catalyst on the pyrolysis product distribution.

2. Experimental

Waste red pepper stems were collected in Jeonnam. The collected biomass was dried and processed into uniform size of 2 mm diameter. The sample particles were then dried further in an oven controlled at 105°C for 24 h. It was reported in a previous study that the waste red pepper stem is composed of 46.4% O, 46.2% C, 5.6% H, and 1.8% N in terms of elemental analysis and of 2.8% moisture, 68.1% volatile matter, 23.3% fixed carbon, and 5.8% ash in terms of proximate analysis.

Si-MCM-48 and Al-MCM-48 were prepared following the method suggested previously [12, 13]. After their synthesis, the catalysts were calcined at 550°C for 3 h. Before each experiment, all the catalysts were dried in a 110°C oven for at least 2 hours.

The characteristics of the catalysts used in this study were examined in a previous study [14]. Nitrogen sorption analysis, X-ray diffraction (XRD), temperature programmed desorption of ammonia (NH_3-TPD), and pyridine FT-IR were used. The acidity of the catalysts was determined by NH_3-TPD analysis. The nature of the acid sites was examined using pyridine as the probe molecule. The surface area, pore volume, and pore size of Si-MCM-48 were 1036 m^2/g, 0.85 cm^3/g, and 2.9 nm, respectively, whereas those of Al-MCM-48 were 864 m^2/g, 0.81 cm^3/g, and 2.9 nm, respectively. The Si/Al ratio of Al-MCM-48 was 40. Al-MCM-48 was shown to have significant amount of Lewis acid sites, whereas Si-MCM-48 had few acid sites.

Pyrolysis experiments were performed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), which is a combination of GC (HP 6890 N Gas Chromatography)/MS (HP 5973 inert Mass Spectral Detector, Agilent Technologies Inc., Santa Clara, CA, USA) and a vertical furnace-type pyrolyzer (Py-2020D, Frontier-Lab Ltd., Fukushima, Japan), to analyze the pyrolysis product directly. A sample cup containing well-mixed biomass-catalyst mixture of 1 mg of pepper stem and 1 mg of catalyst was inserted into the pyrolyzer preheated to 550°C. As the carrier gas that flows through the pyrolyzer, helium gas with the split ratio of 50 : 1 was used. The pyrolysis reaction was allowed to take place for 3 min. The analysis of the species distribution of the vapor-phase pyrolysis product was performed using GC/MS, whose interface temperature was 300°C. The GC oven temperature was increased from 40°C to 300°C at a rate of 5°C/min. Before and after the temperature rising, temperature was maintained at 40°C for 4 min and at 300°C for 10 min, respectively. An HP-5 MS (30 m × 0.25 mm × 0.25 m) capillary column was used for GC/MS. The peaks appearing in the mass spectra were interpreted using the NIST05 library.

3. Results and Discussion

For effective examination of the impacts of the catalyst on the pyrolysis product composition, all the species detected by GC/MS were divided into 8 categories: gas, acids, oxygenates, phenolics, aliphatics (aliphatic hydrocarbons), aromatics, PAHs, and N compounds. Figure 1 compares the product distributions, in terms of the area%, obtained from different catalysis conditions. When the pepper stem was pyrolyzed without catalyst, phenolics were the most abundant products, followed by oxygenates and acids. The production of aliphatics and aromatics was insignificant. When the pyrolysis was performed over MCM-48 catalysts, however, the fraction of phenolics decreased dramatically. On the other hand, the production of all other products, including aliphatics and aromatics, was enhanced. This catalytic effect was more profound for more acidic catalyst, Al-MCM-48. For deeper understanding, the detailed species distributions of oxygenates, phenolics, and aromatics were investigated.

Figure 2 compares the detailed species distributions of oxygenates obtained from different catalysis conditions. It is shown in this figure that levoglucosan, which accounted for a significant fraction in the noncatalytic pyrolysis product, disappeared completely in the catalytic pyrolysis products. On the other hand, the fraction of furans increased dramatically. Because furans are high-value-added products used as organic solvents for the production of medicines, resins, and food and fuel additives, the enhanced production of furans is beneficial [15, 16]. Furans are known to be produced when carbohydrates, such as levoglucosan, are dehydrated over an acidic catalyst [15]. If the acidity of the catalyst is strong enough, furans may be converted further to aromatics [17, 18], which was witnessed in the present study as well when Al-MCM-48, with a higher acidity, led to a more enhanced production of aromatics than that of Si-MCM-48 (Figure 1).

Phenolics were the most dominant product species from the noncatalytic pyrolysis of pepper stem because of the high lignin content of pepper stem (32% according to Won and Oh [19]) but the catalytic reforming reduced the fraction of phenolics to a large extent (see Figure 1). Figure 3 shows the species distribution of phenolics produced under different catalysis conditions. It is shown that the fractions of heavy phenolics mostly decreased as a result of catalytic reforming, while those of light phenols, such as phenol and methyl phenols, rather increased, particularly when Al-MCM-48 was used. The reduction of the heavy phenolic fraction was more significant when Al-MCM-48 was used because of its higher acidity. This can be attributed to the cracking of heavy phenols, produced by the decomposition of lignin, into light phenols and other species, such as aromatics, in the presence of a catalyst with high acidity. Based on their experimental results on the catalytic pyrolysis of *Laminaria japonica* over Al-MCM-48, Lee et al. [11] argued that phenolics were

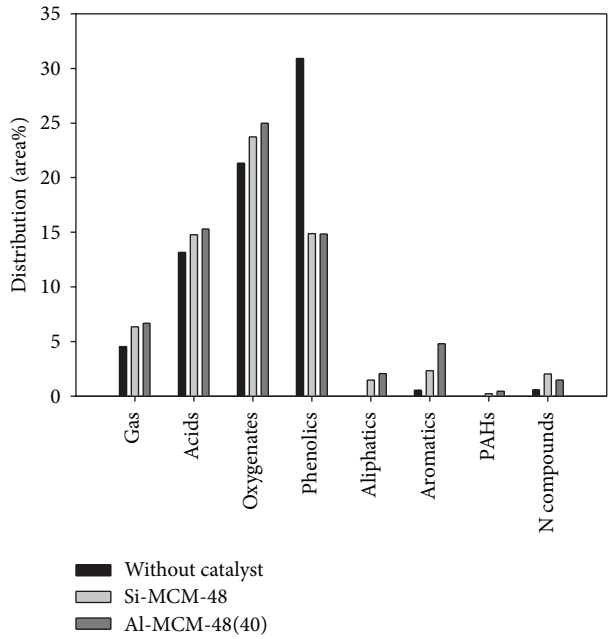

Figure 1: Pyrolysis product distribution obtained under different catalysis conditions.

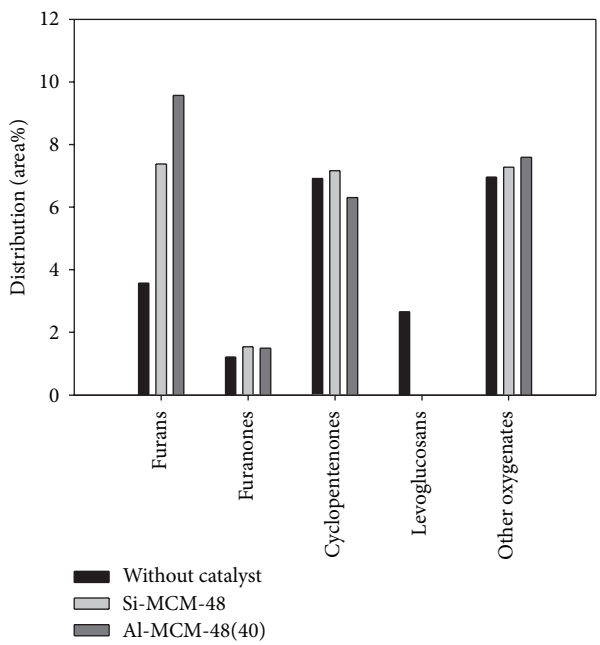

Figure 2: Detailed species distribution of oxygenates obtained under different catalysis conditions.

converted into aromatics on the acid sites of Al-MCM-48, which is in agreement with the result of the present study.

Figure 4 compares the fractions of BTEX species (benzene, toluene, ethylbenzene, and xylene), the most important aromatic compounds, produced under different catalysis conditions. Because these compounds can be used as feedstock materials in petrochemical processes, their fraction in biooil is an important factor determining the value-added of the oil. The production of aromatics is a result of complicated reaction pathways including cracking, dehydrogenation, oligomerization, and aromatization, which require strong acid sites on the catalyst [4, 9]. The production of BTEX was negligible in the case of noncatalytic pyrolysis, whereas it was considerably enhanced when the product oil was reformed over MCM-48 catalysts. In particular, the catalytic effect was much stronger for Al-MCM-48 because of its much higher acidity than that of Si-MCM-48.

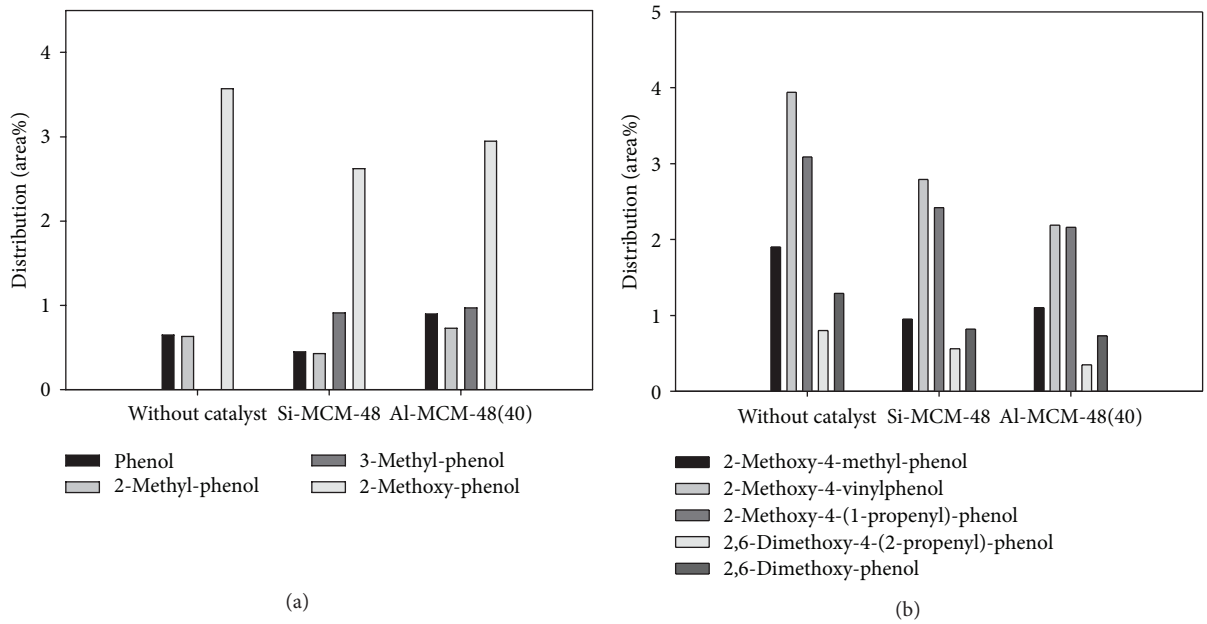

Figure 3: Detailed species distribution of phenolics obtained under different catalysis conditions: (a) small-molecular-mass phenolics; (b) large-molecular-mass phenolics.

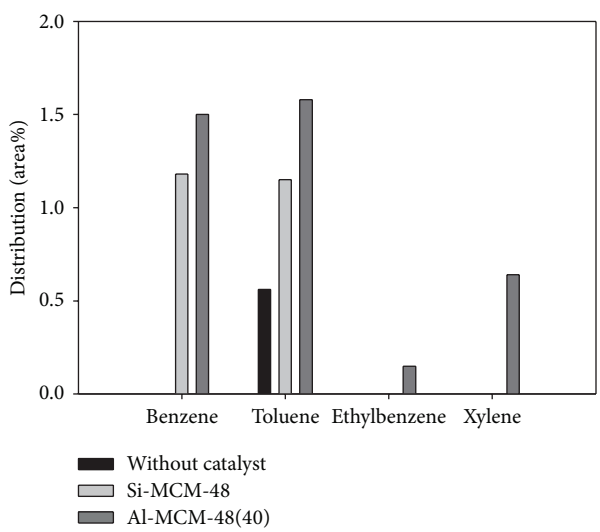

Figure 4: Comparison of the BTEX fractions obtained under different catalysis conditions.

4. Conclusions

Phenolics were the most dominant product species of the noncatalytic pyrolysis of waste pepper stem, while the production of aliphatic and aromatic hydrocarbons was insignificant. When the pyrolysis was conducted over MCM-48 catalysts, however, the production of furans and aliphatic and aromatic hydrocarbons was enhanced considerably, whereas the fraction of phenolics decreased significantly. This catalytic effect was more profound for Al-MCM-48, due to its higher acidity, than for Si-MCM-48. This study suggests that the catalytic pyrolysis over an acidic nanoporous catalyst can be a reasonable way of producing valuable chemicals from waste pepper stem.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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